Electronic Supplementary Information (ESI)

In Situ XAS Study of CoB_i Modified Hematite Photoanodes

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Supporting figures

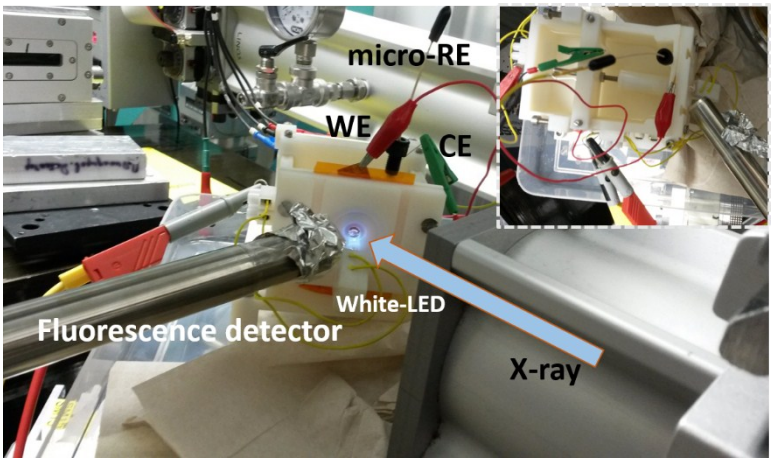


Fig. S1 Photo of the *in situ* PEC fluorescence cell used for XAS measurements. WE, CE and RE are denoted for working, counter and reference electrodes. Inset: top-view of the fluorescence cell. The thin clear polymer window has a high transparency to X-rays and visible light, thus enables XAS spectra to be collected in fluorescence mode.

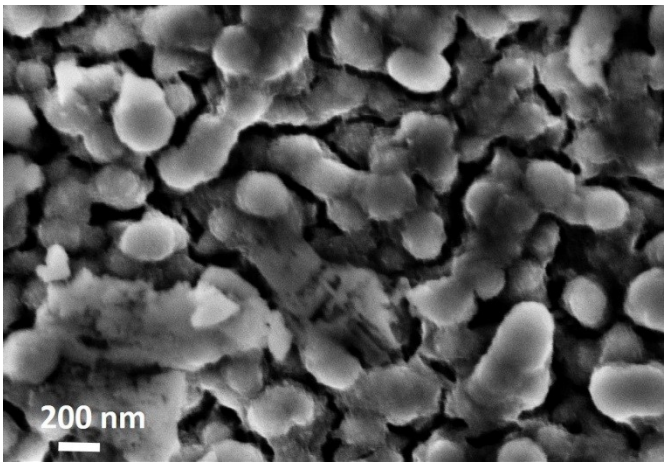
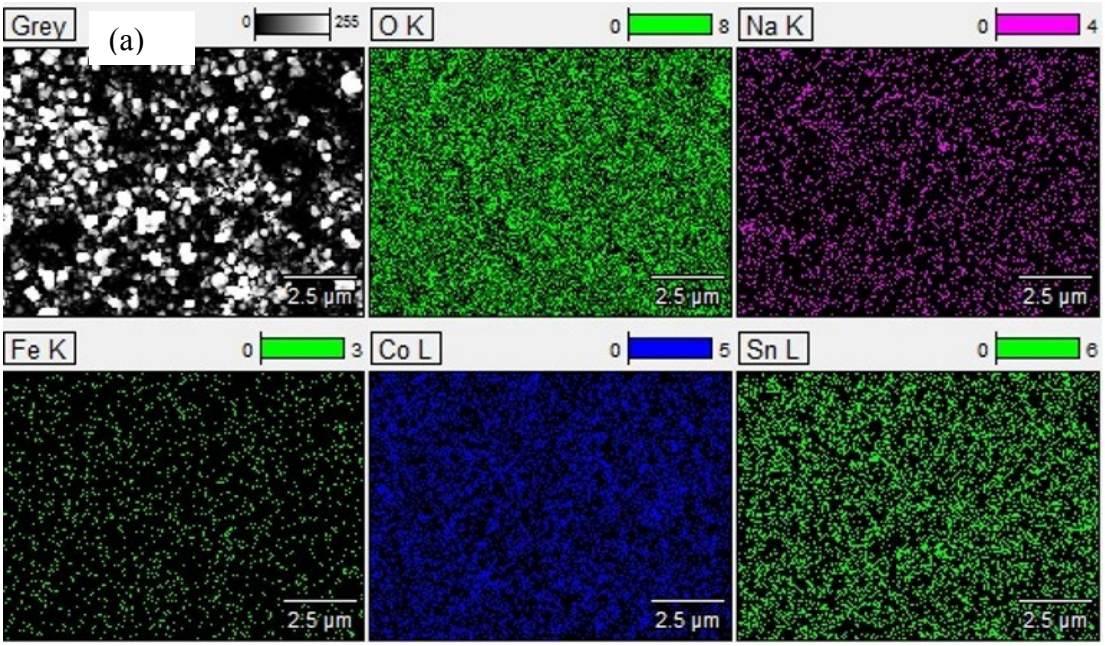
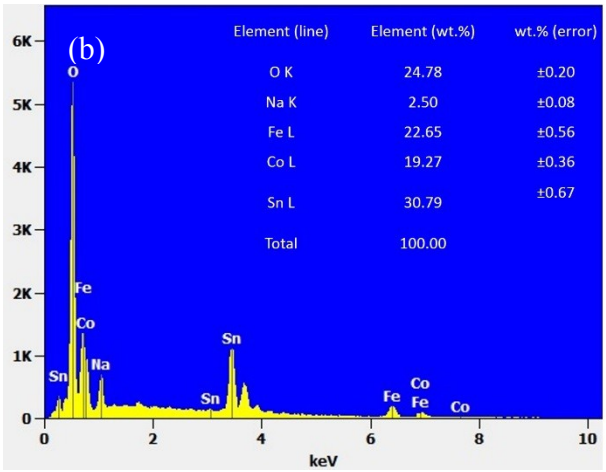


Fig. S2 High resolution-SEM images of the CoB_i modified hematite photoanode.





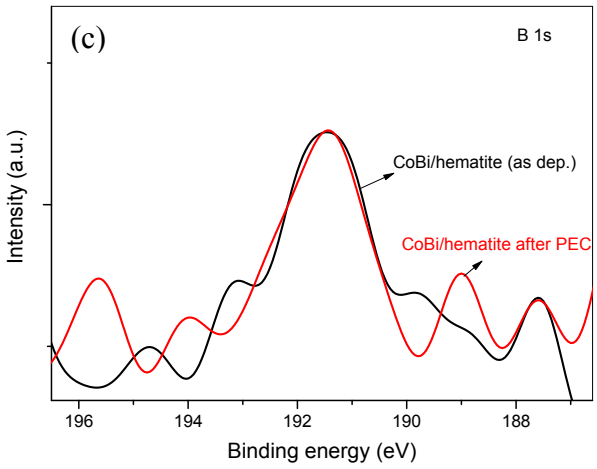


Fig. S3 (a) EDX mapping spectrum and (b) EDX spectrum and composition results of the CoB_i modified hematite photoanode measured a probe beam of 10 keV. (c) XPS B 1s spectrum from the CoB_i modified hematite photoanode. In the B 1s scan (Fig. S3c), the peak at 191.5 eV is consistent with the core level of B^{3+} in borate species.[1]

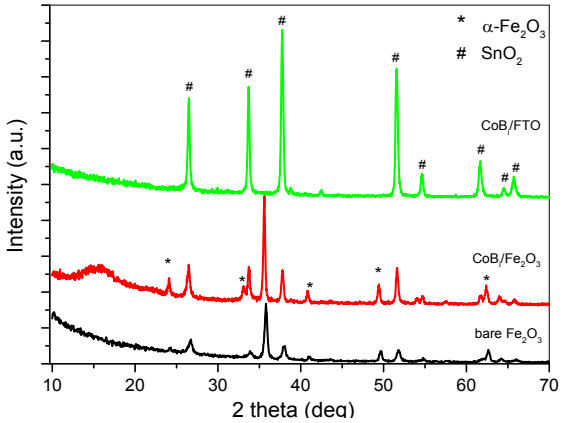


Fig. S4 XRD patterns of CoB_i on FTO, the hematite nanorod array on FTO with and without CoB_i modification. The * denotes Fe_2O_3 (JCPDS 33-0664) and # denotes SnO_2 (JCPDS 46-1088), respectively.

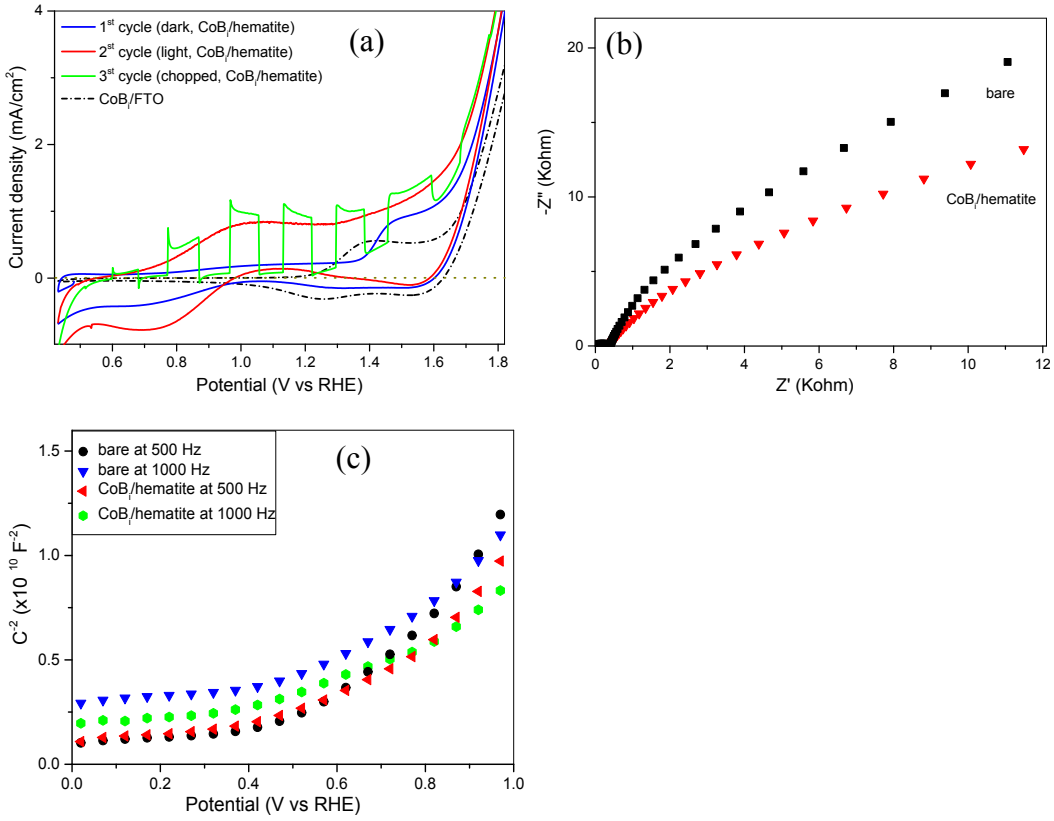


Fig. S5 (a) Cyclic voltammetry (CV) curves of CoBi/hematite under different illumination conditions compared with that of CoB_i/FTO substrate tested in the *in situ* XAS cell under white-LED illumination and (b) Nyquist plots of bare hematite and CoB_i/hematite under 1.0 V vs RHE and dark conditions. (c) Mott-Schottky plots of barehematite and CoB_i/hematite photoanodes tested in the dark under 500 and 1000 Hz.

Fig. S5 shows cyclic voltammetry (CV) curves of the CoB_i modified hematite photoanode under various illumination conditions compared to the CoB_i/FTO substrate. In the forward scan, the CV curve of CoB_i/FTO shows a prominent anodic peak located at 1.41 V. The rapid rise of the current beyond 1.7 V corresponds to catalytic water oxidation. Since the current does not rise exponentially, high resistivity existed in the system. Confined electrolyte between photoanode and polymer window in the cell can be the reason. In the subsequent cathodic scan, a weak peak at 1.53 V and a moderate peak at 1.25 V appear, which are tentatively assigned to the reduction of the Co^{4+} and/or surface Co^{3+} species in the CoB_i film to Co^{3+} or Co^{2+}, respectively.[2] The observed CV features are consistent with previous work.[3] When CoB_i films are photoelectrodeposited on a hematite photoanode, the CV curves clearly show the effect of the CoB_i film. For example, in the forward scan of the dark CV curve (blue), a prominent anodic hump located at 1.50 V is observed, similar to that of the CoB_i/FTO but with a slightly anodic shift. In the light and chopped light CV curves, the photo effect as well as the CoB_i modification effect are clearly visible.

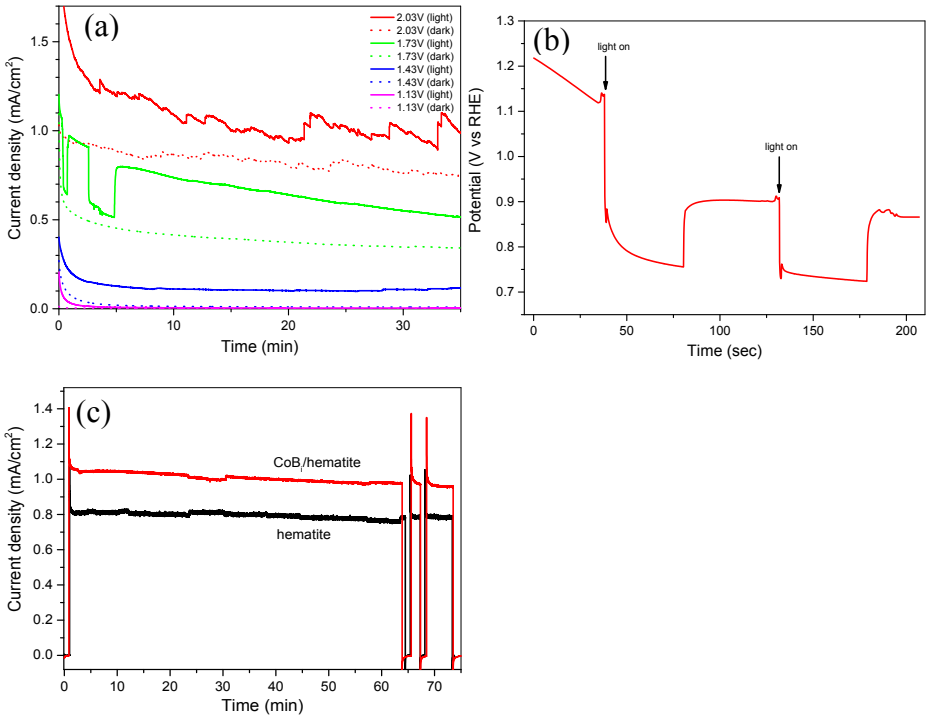


Fig. S6 (a) Photocurrent–time (I–t) curves of hematite photoanodes under different potentials and light conditions obtained in XANES tests. (b) Open circuit potential (OCP) curve of a CoB_i/hematite film obtained under dark and light. (c) Stability test of bare and CoB_i modified hematite photoanodes tested at 1.23 V vs RHE in 0.1 M NaB_i (pH 9.2).

Fig. S6 shows the light and potential effect during the *in situ* X-ray absorption near edge fine structure (XANES) tests. The jumps and noisy behavior are due to the oxygen gas generation which affected the active surface area, thus affecting the photocurrent density. It can be seen that the CoB_i cocatalyst modified photoanode is relatively stable. The gradually degrading current density can be due to the poor conductivity of the electrolyte or due to oxygen bubbles which reduced the active surface. Fig. 6b shows an OCP curve of a CoB_i modified hematite film. The OCP shifts to a more negative potential under illumination which indicates the flattening or a downward band bending typical for an n-type semiconductor-electrolyte junction. It is reported that the flat band potential for hematite lies around 0.4 - 0.8 V vs. RHE.[4] For any potential more anodic than the flat band potential, the upwards band bending drives photogenerated holes towards the photoelectrode/electrolyte interface.

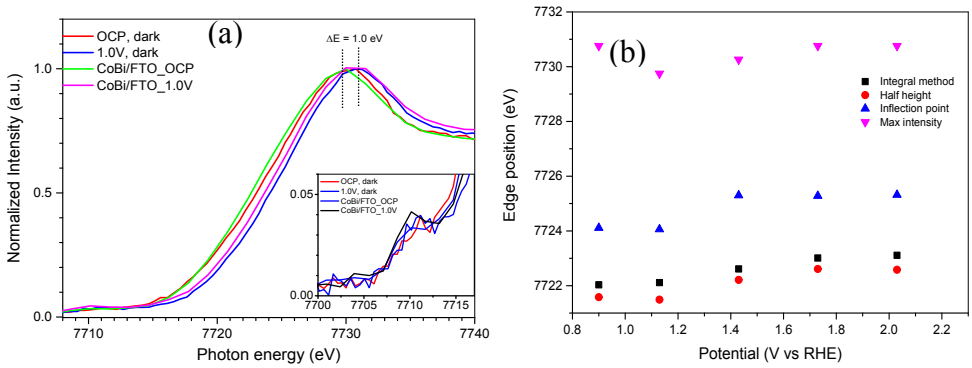


Fig. S7 (a) Normalized XANES spectra at cobalt K-edge of CoB_i/hematite compared with CoB_i film on FTO substrate. (b) Edge position of Co in CoB_i/hematite under dark obtained from different edge estimation methods.

References

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2. R. L. Doyle, I. J. Godwin, M. P. Brandon and M. E. G. Lyons, *Phys. Chem. Chem. Phys*., 2013, **15,** 13737-13783.
3. Y. Surendranath, M. Dinca and D. G. Nocera, *J. Am. Chem. Soc*., 2009, **131**, 2615-2620.
4. B. Iandolo, H. Zhang, B. Wickman, I. Zoric, G. Conibeer and A. Hellman, *RSC Adv.,* 2015, **5**, 61021-61030.